Studies on Monomolecular Films. IX. The Effect of Dissolved Dyes on the Monolayer of Stearic Acid

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Introduction

In the preceding two papers(1),(2) the effect of metallic ions on the monolayer of stearic acid was reported. There it was suggested that such metallic ions as thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel in the substrate formed stearate of a complicated high-molecular structure in the film. It may be expected that some contribution to the confirmation of this suggestion will be obtained by studying the effect of the substance of a large molecule dissolved in the substrate on the monolayer of stearic acid formed on it. For this purpose dyes are considered suitable because the molecules of the dyes are usually large, sometimes forming micelles in a solution, and, in addition, they have one or more ionizable groups which are expected to interact with a polar group of stearic acid. For this reason it has been attempted in this experiment to investigate the interaction between some dyes in the substrate and stearic acid in the film and to compare the result with the effect of such metallic ions as mentioned above. Furthermore, since some dyes are known to be remarkably surface active and their surface chemical properties have been studied in connection with the adsorbed films,(3) foams,(4) etc., it is interesting also for the purpose of studying the surface chemical properties of dyes with regards to their molecular structure to investigate the interaction between dissolved dyes and insoluble films.

Experimental

Dyes used in this experiment were conventionally classified according to their molecular structure into three groups, namely those of acidic, basic and amphoteric ones. As acidic dyes scarlet red and phloxine, as basic dyes chrysoidine, crystal violet and night blue and as amphoteric dyes methyl orange, congo red and trypan red were chosen. Of all these dyes crystal violet, methyl orange and congo red were especially purified by salting out(5) or recrystallization. Comparison of the effect of a commercial dye with that of a purified one on the monolayer of stearic acid gave no essential difference between them, and so the rest of the dyes were used without special purification. Each of these dyes was dissolved in water to the concentration of 10^{-2} mol/l. and aged for about ten days before use. The solution was diluted to 10^{-4} mol/l. when it was used, and the monolayer of stearic acid was spread on the surface of this solution and the pressure∼area curve was measured in the same way as described already.(6) The hydrogen ion concentration of the dye solution was varied from 1.5 to 10 using hydrochloric acid and ammonium hydroxide. Here the use of ordinary buffer salts was avoided for controlling *p*H because of the disturbing effect produced by buffer ions as mentioned in the preceding paper.(1) The film experiment was carried out at room temperature.

Results

As to the effect on the stearic acid monolayer, some dyes were remarkable in their action in a *p*H range of the solution proper for each dye, while the effect was imperceptible with other dyes throughout the whole range of *p*H in the present experiment.

(1) **Acidic Dyes.**—Scarlet red showed no effect on the pressure∼area relation of the monolayer of stearic acid spread on the surface of the solution throughout the whole range of *p*H, covering from 1.5 to 10, while phloxine modified it considerably in the solution of the acid region. In Fig. 1 the area per molecule of stearic acid at the pressure of 2 dynes/cm. with or without the dyes in the underlying

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(1) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951).

(2) R. Matuura, This Bulletin, **24**, 278 (1951).

(3) K. S. G. Doss *Kolloid-Z.* **84**, 138 (1938); **86**, 205 (1939). **87**, 272 (1939).

(4) M. Nakagaki, This Bulletin, **22**, 201 (1949); **23**, 48, 105 (1950).

(5) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc. A*, 131 576 (1931).

(6) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayashi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1 (1948).

solution is plotted against its pH. It can be seen that in the presence of phloxine the curve shows a sharp maximum at pH 3.5. It was found that even in the absence of the monolayer of stearic acid the phloxine solution formed rigid adsorbed films of its own at the neighborhood of this pH, and they appear practically insoluble, showing rather a large surface pressure. The question arose that the remarkable expansion of a stearic acid monolayer might come from this adsorbed film of the phloxine solution, but the comparison with the blank experiment showed that it was caused considerably by the interaction between phloxine and stearic acid and could not be explained merely by a simple additive effect of both films.

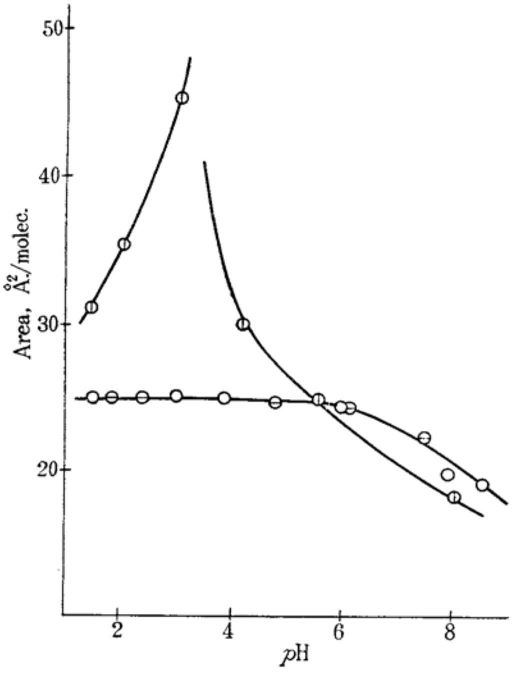

Fig. 1.—Area ∼ pH curves of monolayer of stearic acid on water containing acid dyes: ○, without dye; ⊖, scarlet red; ⦶, phloxine.

(2) **Basic Dyes.** —Both chrysoidine and crystal violet made the monolayer of stearic acid expand in the solution of the alkaline region as shown in Fig. 2. In the case of night blue the expansion of the monolayer of stearic acid was very remarkable, but this dye formed rigid adsorbed films of its own from especially the alkaline solution, just as phloxine did from the acid solution. The result with night blue is not shown in Fig. 2. A trouble occurred that the solutions of crystal violet and night blue remarkably wetted the paraffined wall of the tray so that the water in the tray overflowed from the edges on compression and the film experiment became impossible. This was largely avoided by using the solution whose concentration was 10^{-5} mol/l. The result with crystal violet shown in Fig. 2 is that obtained using this dilute solution, the film area being that at the surface pressure of 15 dynes/cm. In the case of chrysoidins the concentration of the solution was 10^{-4} mol/l., and the film area

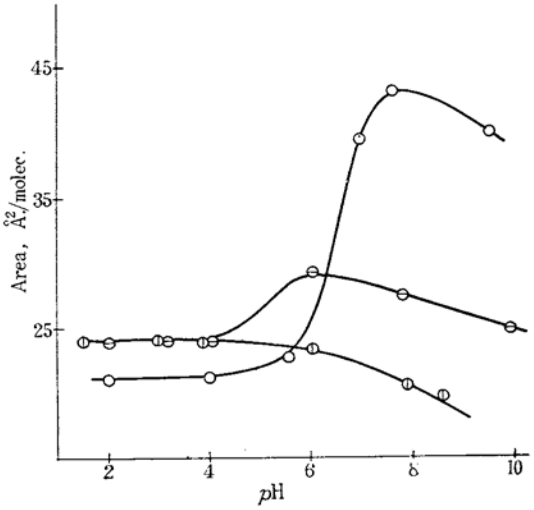

Fig. 2.—Area∼pH curves of the monolayer of stearic acid on water containing basic dyes: ○, crystal violet (area at 15 dynes/cm.); ⊖, chrysoidine; ⦶, without dye.

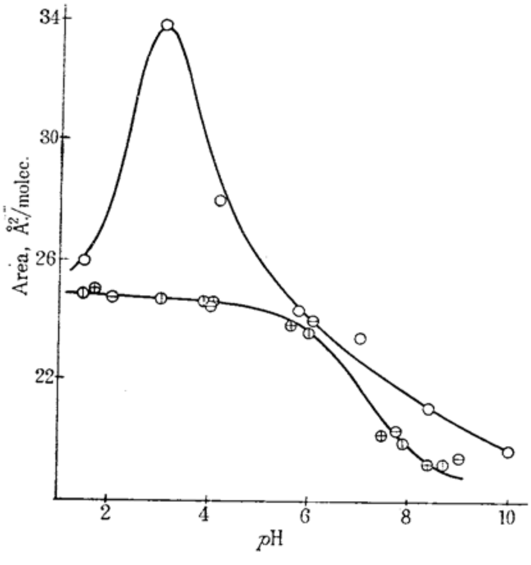

Fig. 3.—Area∼pH curves of the monolayer of stearic acid on water containing amphoteric dyes: ○, congo red; ⊕, methyl orange; ⊖, trypan red; ⦶, without dye.

was that at 2 dynes/cm..

(3) **Amphoteric Dyes.**—It was found that methyl orange and trypan red gave no measurable effect on the monolayer of stearic acid in the *p*H range from 2 to 10, while congo red affected it remarkable when the substrate solution was acidic, as shown in Fig. 3. The film area in Fig. 3 was that at the surface pressure of 2 dynes/cm. It is seen that the curve for congo red shows a maximum at *p*H 3. As the solution becomes more acidic, congo red reduces its solubility and finally precipitates.

Discussion

The result of the present experiment shows that some dyes, when dissolved in the substrate, remarkably expand the monolayer of stearic acid spread on it. It is probable that this comes from the interaction between dyes in the substrate and stearic acid in the film. Here it is of importance to seek for the explanation for this interaction in terms of the molecular structure of the dyes. In the interaction between the dye and stearic acid electric forces due to polar and ionic groups and van der Waals force between nonpolar groups will play an important rôle. Electric forces, of course, are affected by the hydrogen ion concentration of the solution, while van der Waals force is independent of *p*H. Because of the presence of dye ion and stearate ion, both anion, a repulsion will act between the acidic dye and stearic acid in the solution of the alkaline region. This repulsion will disappear in the acid region and the dye will have a possibility of being adsorbed by van der Waals force to the surface of the stearic acid film. This may perhaps be taken as the explanation of the remarkable expansion of the monolayer of stearic acid on the acid solution of phloxine. In the case of scarlet red the ionic repulsion will be much greater because of its strongly ionizable $-SO_3Na$ group and weak van der Waals attraction due to a small size of the molecule. This leads to the failure in adsorption to the monolayer of stearic acid throughout the whole range of *p*H in the present experiment. The remarkable expansion of the monolayer of stearic acid in the presence of congo red at *p*H 3 may also be explained by van der Waals adsorption of the dye to the monolayer. That is, at this *p*H, being the isoelectric point of congo red, the electric repulsion will be the least between the dye and stearic acid due to the lack of the electric charge as a whole, and the van der Walls force will become the dominant one. In case of trypan red, although the molecule is large, five sulfonic groups will act to shift its isoelectric point towards more acidic side, which prevents the adsorption from taking place. It might be expected that here the adsorption by the van der Waals force will occur if the solution is rendered much more acidic than that in the present experiment.

The situation is different in the case of basic dyes. They produce dye cations which are, presumably, capable of combining with stearic acid to form stearates. The degree of ionization of the basic dye becomes larger while that of stearic acid becomes smaller as *p*H of the solution decreases, and, consequently, it is expected that the adsorption becomes most pronounced at a certain *p*H value of the solution. This is confirmed by the present experiment, as shown in Fig. 2, where it is seen that the maximum expansion of the stearic acid monolayer occurs at *p*H 6 in the case of chrysoidine and at *p*H 7.8 in the case of crystal violet. In order to know further the significance of ionic interaction between basic dyes and stearic acid, the effect of crystal violet on the monolayer of cetyl alcohol was investigated. The condition of the experiment was the same as in the case of the monolayer of stearic acid. The result is shown as area∼*p*H curves in Fig. 4. It should be noted that the expansion of the monolayer of cetyl alcohol is much smaller

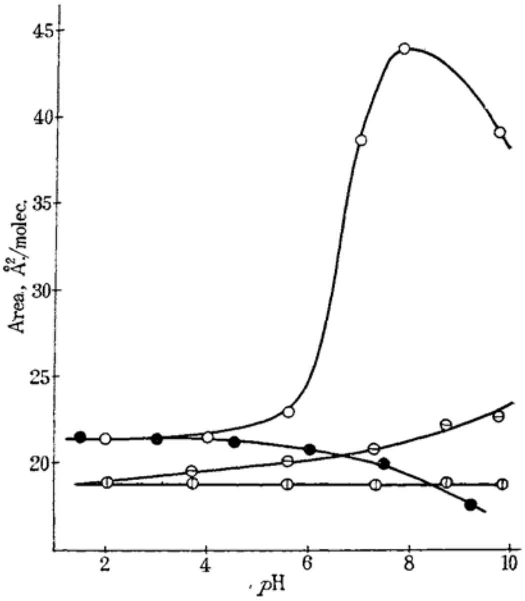

Fig. 4.—Comparison of the effect of crystal violet on the film area (at 15 dynes/cm) of stearic acid with that of cetyl alcohol: ○, stearic acid with dye; ●, stearic acid without dye; ⊖, cetyl alcohol with dye; ⦶, cetyl alcohol without dye.

than that of stearic acid in the presence of crystal violet. This is explained by the fact that cetyl alcohol is much less ionizable than stearic acid and so ionic interaction, a chief factor of the mutual interaction considered above, is much weaker between cetyl alcohol and crystal violet than between stearic acid and crystal violet. Such an ionic interaction has also been confirmed in the case of proteins and some dyes.(7)

It should be emphasized here that the mechanism of the interaction between dyes and stearic acid is fairly complex in nature, involving at least the ionic interaction and van der Waals force. The latter is also considered as a main factor determining the solubilization of dyes by detergents, the phenomenon which became to draw attention of many investigators recently.(8) The author reported in the preceding paper the special interaction between stearic acid and such metallic ions as aluminum, thorium, etc. Comparing this with that between stearic acid and dyes studied in the present experiment we can find some similarities as well as differences in the mechanism underlying them. It may be mentioned that the basic dyes react with stearic acid in a similar manner as thorium and aluminum ions do with stearic acid as far as the expansion and the complex structure of the resulting film are concerned. This view can also be confirmed by the experiment of wettability carried out by Inaba(9) of our laboratory.

Summary

The interaction between the dyes dissolved in water and the monolayer of stearic acid spread on it was studied and discussed. It was shown that a remarkable expansion of the monolayer of stearic acid in the presence of phloxine and congo red was explained chiefly by the van der Waals adsorption, while that in the presence of basic dyes was explained chiefly by the ionic interaction. It was suggested that the interaction between basic dyes and stearic acid was analogous in some respects to the formation of soaps of such metals as thorium, aluminum, etc.

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(8) H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

(9) A. Inaba, to be published recently.